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On the phase transition and excitations in liquid helium

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With 3 figures in the text

The thermodynamic properties of liquid helium at the pressure of its saturated vapour are best surveyed by distinction of three temperature ranges. In the lowest range for $T < 0.6°\mathrm{K}$ the properties are those characteristic of He II. According to measurements by the Leiden group [1, 2] the energy is proportional to T^4 in accordance with the energy of solids at low temperatures. In the highest range, say $T > 2.5°\mathrm{K}$, the liquid is in the state of He I. Here the energy increases approximately linearly with T^2. In this range the properties are, as pointed out by the present author [3], similar to the properties of a condensed highly degenerate Fermi gas. In the range in between from about 0.6 to about 2.5°K it is possible to follow the transition from He II to He I which has its steepest gradient at the λ point, 1.826°K.

The remarkable mechanical, thermal and thermo-mechanical properties of helium in the range of transition below the λ point have been attacked theoretically in somewhat different ways by Tisza [4], H. London [5], Landau [6], and others on the assumption that helium in the states of transition is a mixture of two types of liquids. The aim of the present paper is to show how further information about the transition can be obtained in a very simple way by considering helium, in the state of transition, as a mixture of two components with the typical properties of He II and HeI as we know them from the measurements below 0.6 and above 2.5°K.

We shall consider the variations with temperature of the energy E and the entropy S per mole at the pressure of the saturated vapour. The experimental data are obtained from measurements of the atomic heat capacity C. For the range below 0.6°K we have used the results of Wiebes, Niels-Hakkenberg and Kramers [2]. For the range from 0.6°K to the λ point we have used the smoothed values tabulated by Kramers, Wasscher and Gorter [1]. Above the λ point the data are from diagrams on basis of the measurements by Keesem and Miss Keesom [7, 8], and Keesom and Clusius [9].

The thermal energy content per mole at vapour pressure is given by

$$E = \int_0^T C\,dT - \int_0^T p\,dV, \tag{1}$$

where p is the pressure of the saturated vapour and dV the thermal volume expansion. The second term is small and within the limits of the experimental uncertainty of the first. The computed values for E are given in the second column of Table 1 and

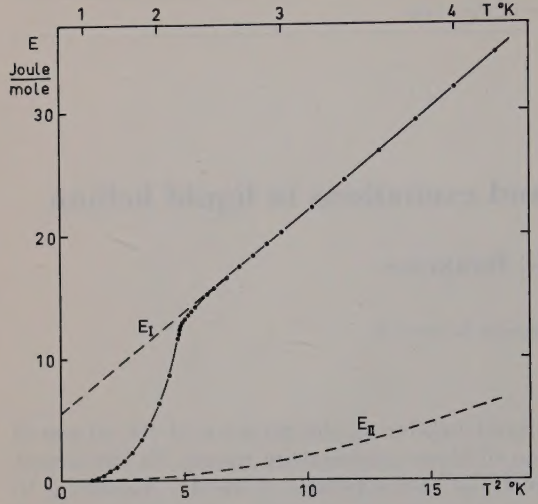

Fig. 1. Energy as a function of the square of the absolute temperature.

shown as a function of T^2 in Fig. 1. The state of He I is described by the approximately straight line above the λ point in the figure and by the empirical formula

$$E_{\mathrm{I}} = 5.50 + 1.57\, T^2 \text{ Joule/mole.} \tag{2}$$

For He II the measurements below 0.6°K [1] give the empirical formula

$$E_{\mathrm{II}} = 0.0204\, T^4 \text{ Joule/mole.} \tag{3}$$

Values of E_{I} and E_{II} according to these equations are given in the 3rd and 4th columns of Table 1.

If we assume that helium in the range of transition is a mixture of He I and He II, each component having the energy obtained by an extrapolation of the formulae (2) and (3) as shown by the dashed lines in Fig. 1, then the simplest assumption that can be made for the energy E in this range is

$$E = x E_{\mathrm{I}} + (1 - x) E_{\mathrm{II}}, \tag{4}$$

where x and $(1 - x)$ are the fractions of atoms in the two states. We may draw attention to the fact that this assumption means that all atoms belong to one or the other of the two states, so that there is not a third fraction of atoms, for instance at boundaries, with a third type of energy. The results will justify this simplification.

Inserting values of E, E_{I}, and E_{II} for different temperature in (4) we obtain the values of x given in the 5th column of Table 1. These values give the fractions of He I in the mixture. It is interesting to compare these fractions with the fractions ϱ_n/ϱ of the liquid taking part in internal friction according to the measurements by Andronikashvili [10]. As Andronikashvili has assumed the frictional part to be 1 at the λ point his values have to be compared with x/x_λ where $x_\lambda = 0.907$ is the value of x obtained for the λ point. The results for x/x_λ in the 6th column of the table are in excellent agreement with the values of Andronikashvili, shown in the 7th column,

Table 1. Energy of liquid helium in the transition range.

1	2	3	4	5	6	7
°K	Joule/mole					
	E	E_{I}	E_{II}	x	x/x_{λ}	ϱ_n/ϱ
1.0	0.056	7.07	0.020	0.005		
1.1	0.113	7.40	0.030	0.012		
1.2	0.214	7.76	0.042	0.022		
1.3	0.379	8.15	0.058	0.040	0.04	0.05
1.4	0.605	8.58	0.078	0.066	0.07	0.07
1.5	1.014	9.03	0.103	0.102	0.12	0.12
1.6	1.548	9.52	0.134	0.151	0.17	0.17
1.7	2.282	10.04	0.170	0.214	0.24	0.24
1.8	3.266	10.59	0.214	0.294	0.32	0.32
1.9	4.545	11.17	0.266	0.393	0.43	0.43
2.0	6.262	11.78	0.326	0.518	0.57	0.56
2.1	8.605	12.42	0.397	0.691	0.74	0.75
2.186				0.907	1.00	1.00
2.2	12.03	13.10	0.478	0.915		
2.3	13.40	13.81	0.571	0.970		
2.4	14.35	14.54	0.677	0.986		
2.5	15.26	15.31	0.797	0.997		

which are taken from the smoothed curve on page 395 in Mendelsohn's survey on liquid helium in *Handbuch der Physik* [11].

We next turn to the entropy, obtained from the equation

$$S = \int_0^T \frac{C}{T}\, dT. \tag{5}$$

Its dependence on temperature appears from the diagram of Fig. 2 and the second column of Table 2. The experimental results above 2.5°K are satisfied by the expression

$$S_{\mathrm{I}} = 2 \times 1.57\, T = 3.14\, T \text{ Joule/mole deg} \tag{6}$$

and the results below 0.6°K by

$$S_{\mathrm{II}} = \tfrac{4}{3}\, 0.0204\, T^3 = 0.0272\, T^3 \text{ Joule/mole deg.} \tag{7}$$

The computed values are collected in the 3rd and 4th columns of Table 2. The equations (6) and (7) are thermodynamically connected to the equations (2) and (3), respectively.

If there could only be a macroscopic mixture of He I and He II the entropy should be given by a formula of the same type as the formula (4) for the energy of the mixture. This, however, should give $x = 0$ below and $x = 1$ above a transition point of the first order. The fact that the transition is of higher order shows that there must exist a finite entropy of mixing, which means that at least one of the

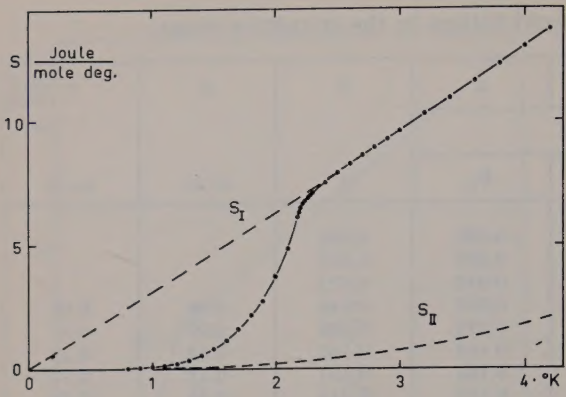

Fig. 2. Entropy as a function of the absolute temperature.

Table 2. Entropy of liquid helium in the transition range.

1	2	3	4	5
°K	Joule/mole × degree			
	S	S_I	S_{II}	ΔS
1.0	0.068	3.17	0.027	0.025
1.1	0.121	3.49	0.036	0.045
1.2	0.208	3.80	0.047	0.077
1.3	0.341	4.12	0.060	0.120
1.4	0.527	4.44	0.075	0.166
1.5	0.787	4.76	0.092	0.218
1.6	1.136	5.07	0.111	0.274
1.7	1.580	5.39	0.134	0.32
1.8	2.140	5.71	0.159	0.35
1.9	2.84	6.02	0.19	0.36
2.0	3.72	6.34	0.22	0.32
2.1	4.89	6.66	0.25	0.16
2.2	6.47	6.97	0.29	0.07
2.3	7.09	7.29	0.33	0.00
2.4	7.48	7.61	0.38	—
2.5	7.85	7.93	0.43	—

two components of the mixture must appear as aggregates containing a limited number of atoms. Accordingly the entropy of the mixture may be written

$$S = xS_{\mathrm{I}} + (1-x)S_{\mathrm{II}} + \Delta S, \tag{8}$$

where ΔS is the entropy of mixing. Using the values of x from Table 1 we obtain the values of ΔS in the 5th column of Table 2.

In Fig. 3 the entropy of mixing ΔS is plotted as a function of the fraction x of He I. For small values of x, that is at the low temperature side, ΔS fits to the curve, which describes a mixing entropy of the type

$$\Delta S = -\frac{R}{n}\, x \ln x, \tag{9}$$

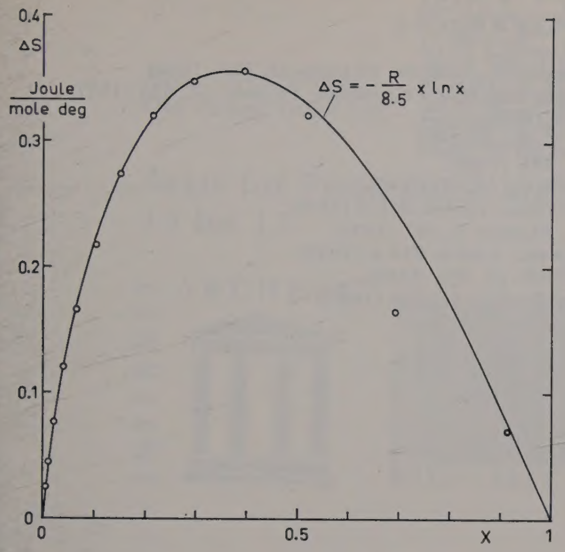

Fig. 3. Entropy of mixing ΔS as a function of the fraction x of atoms in the state of He I.

where R is the gas constant and n has the value 8.5. The estimated limits of uncertainty owing to uncertainty in the specific heat is ± 1. We thus have

$$n = 8.5 \pm 1. \tag{10}$$

For values of x between 0.5 and 1, that is near to the λ point, the experimental uncertainty of ΔS is especially high.

A thinkable interpretation of this result is that the excitations introducing He I in He II, which by Landau [6] were interpreted as "rotons", are some kind of molecules covering about 8 atoms. We may for instance think of eight atoms at equal distances around a central interspace or of a central atom and its nearest neighbours. In the first case all atoms of the molecule have equivalent positions so that the simple form of equation (4) is fully justified. In the second case all but the central one of the atoms are equivalent and equation (4) should be at least approximately valid.

As has been discussed in some detail in the preceding paper [3], the energy and entropy of He in the state of He I are such as could be expected for a condensed highly degenerate Fermi gas. On first sight this seems to be rather inconceivable from a theoretical point of view. The theoretical difficulty would be overcome if it could be found a reason for the movements of the helium atoms in the molecules to obey the Pauli exclusion principle.

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